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Enhancing The Activity of Pyridin-2-one derivatives formulated with Nano Synthetic Surfactant on Two Spotted Spider Mite Infesting Cotton in Egypt

Naira S. Elmasry*, Heba M. Nasr, and Sheren A. Shoman
Researcher in Plant Protection Res. Institute, Agric. Res. Center, Egypt.
E-mail* : nairaelmasry@gmail.com , hebanasr112@gmail.com; sherinshoman@gmail.com

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ABSTRACT

During the year 2021/2022, the effect of two pyridin-2-one derivatives which belong to cyano acetamides and their modified formulations was studied to control the two-spotted spider mite, *Tetranychus urticae Koch*. We prepared and characterized pyridin-2-one derivatives (as active Ingredients). The structures of the products were determined by IR spectrum, Mass spectra,^{1}H NMR spectrum and melting point. Five concentrations of 1-(4-Acetylphenyl) -4-(4-(dimethylamino)-phenyl) -6-hydroxy -2-oxo-1,2dihydro pyridine-3,5dicarbonitrile; (9.25,37.5,125, 250 and 500ppm), from 1-(4-Acetylphenyl)-6-amino-4-(4-(dimethylamino)-phenyl)-2-oxo-1,2dihydro pyridine -3, 5-dicarbonitrile; (12.5, 25, 50, 100 and 200 ppm) and from Congest 15% CS (5,15,25,35 and 45ppm) and their modified mixture solutions with 5-(benzo[d]thiazol-2-yl) -3-phenyl-2-thioxo -2,3-dihydrothiazol -4-aminiumN,N,N trimethyl hexadecan-1-aminium bromo trichloro cuprate (0.1g) were applied under semi-field conditions against two-spotted spider mite. The two derivatives were modified by using nano cationic surfactant to increase their toxicity effect on *T.urticae* Koch. Also, the toxicity effect of Congest 15% CS (as a traditional chemical pesticide) and its modified solution by the tested new surfactant were carried out under semi-field conditions. The result showed that the two formulated pyridin-2-one materials with the nano surfactant additive were more effective than Congest 15%CS only solution. The values (19.59, 23.77 and 28.27 ppm) of LC_{50} were calculated for Congest 15% CS and the two pyridin-2-one derivatives a respectively and LC_{50} values were decreased to (0.43, 1.96 and 5.166), also the lethal time (LT; hours) were significant decrease after adding the new nano synthetic surfactant to the tested pesticide and chemicals respectively.

INTRODUCTION

The two-spotted spider mite is a phytophagous pest that can propose a serious loss in yield of many agricultural crops such as fruits, cotton, vegetables, and ornamentals such as roses, carnations, and gladiolus (Singh, 2015). Spotted spider mites species that has been debatable in its taxonomic status. The body of a spider mite is separated into two distinct parts: (1) the gnathosoma is only the mouth parts and (2) the idiosoma includes the head, the body and parallels, abdomen, and thorax. The first larva stage (after the egg hatching) has six legs. Then, the adult larvae have eight legs. All spotted spider mites species have sucking

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mouth parts (as a sharp needle). They feed by their sucking mouthparts penetrating the tissue of the plant. The mites are found on the down surface of the leaf. Also, the yarn fine strands of webbing on the host plant. Usually, mites are controlled with traditional chemical pesticides such as organophosphates, neonicotinoids, carbamates and pyrethroids. Singh *et al.*, 2017 evaluated the efficacy of mineral oils and six pesticides (imidacloprid, dicofol, propargite, dimethoate and fenazaquin) against two-spotted red spider mite. Abdelmaksoud *et al.*, 2020 evaluated the activity of different traditional pesticides on strawberry plants. The tested pesticides were Solo 24% SC (Bifenazate), Concor 24% SC (Spirodiclofen), Arbus 12% SC (Chlorfenapyr + Emamectin benzoate), Top9 (Chitosan 0.1%), Biomectin 5% EC (Abamectin) and Congest 15% CS (Abamectin + Imidacloprid) against two-spotted spider mite, Tetranychus uriticae Koch on strawberry plants. But the wide use of these synthetic traditional pesticides causes an increase in strains resistant to many insecticides (Cao et al.,2008). Therefore, it is important to improve the use rate of pesticides and extend their duration of activity in the environment (Khot, *et al.*, 2012; Wang, *et al.* 2014; Cui, *et al.*, 2015, and Liu *et al.*, 2016). The application of nano additives to pesticides leads to minimizing the environmental damage by classical pesticides, more effective targeting pests, decrease quantities of applied pesticide of the spray on the surface. These pesticides in nano-sized mostly progress environmental and human safety and lower pest control costs. Abdel-Halim and Kalmosh evaluated the efficiency of abamectin 1% EC (nano-emulsion) against T. uritcae Koch (Abdel-Halim and Kalmosh, 2019). While using new technology, the safety of the user and its effect on the environment have to be considered (Gopal, *et al.*, 2012).

The surfactants as chemical additives to pesticide spray solutions are enhanced their efficacy. Various adjuvants are increasing the adsorption of target plant foliage, to active ingredients. The penetration of pesticides is regarding the changing in physicochemical properties of the active ingredients (Ferna´ndez Cirelli, *et al.*, 2008). These chemical additives decrease the number of active compounds needed, so decreasing pollution and cost. There are several types of applied surfactants on pesticide spray solutions according to the nature of the hydrophilic group including cationic, anionic, amphoteric and non-ionic surfactants (Castro, *et al.*, 2014). The most widespread type of cationic surfactant additives is the quaternary ammonium compounds (QAC). They contain at least one hydrophobic hydrocarbon chain (as methyl, alkyl groups, or benzyl groups) connected to a positively charged nitrogen atom (Ivankovic and Hrenovic,2010). Cationic surfactant additives have gained interest because of their high absorptivity to a wide set of surfaces, also they are used as flotation agents. The evolution of a new surfactant-based system as an activator for active ingredients is a key factor in increasing process efficiency and decreasing cost, energy and raw material. In recent years, there is a public pressure to decrease the number of pesticides released into the environment. The new synthetic active ingredients with nano additives are applied to improve the activity and persistence of the active ingredient (Knowles, 2008). Also, the pesticide additives have a sub-lethal effect and potential biological control of the tested pests but also, they affect beneficial organisms in agro ecosystems. Thus, the new studies go towards making new synthetic active ingredients with nano additives as a new window for the safe and specific application (Niedobová, *et al.*, 2016).

MATERIALS AND METHODS

1. Tested Insecticide*:*

Congest 15% CS (Abamectin+Imidacloprid). Its chemical class is avermectin with neonicotinoid and its applied rate is 35cm^3/100L in the field (Abdelmaksoud, *et al.*, 2020).

2. Synthesis and Characterization of Pyridin-2-one Derivatives (Active Ingredients):

The reaction was started by adding 0.0015 mole of N-(4-acetyl phenyl)-2-cyanoacetamide (1). which was prepared in dry benzene by treatment of p-aminoacetophenonewith1-canoacetyl-3,5-dimethylpyrazole as strong cyanoacylating reagent according to the reported procedure (Yermolayev *et al.*, 2009) with a few catalytic drops of tri ethyl amine as a basic condition to a solution of 0.0015mole arylidene ethyl acetate (2) similarly arylidene malono nitrile (4) in 20ml ethanol solution. The mixture was refluxed with heating for 3 $hr_{s.}$, then set to cool at room temperature. The solid product was filtrated, then washed with ethanol, and recrystallized by EtOH/DMF to give pyridin-2-one derivatives as shown in Figure (1). The derivative 1 was (1-(4-Acetylphenyl) -4-(4-(dimethylamino)-phenyl) -6-hydroxy-2-oxo-1,2-dihydropyridine-3, 5-dicarbonitrile (3)) with yield 75%, and the derivative 2 was (1-(4-Acetylphenyl)-6-amino-4-(4-(dimethylamino)-phenyl)-2-oxo-1,2 dihydropyridine-3,5-dicarbonitrile (5)) with yield 65% respectively. The structures of the products were determined by IR spectrum, Mass spectra, ^{1}H NMR spectrum and melting point as shown in Table (1).

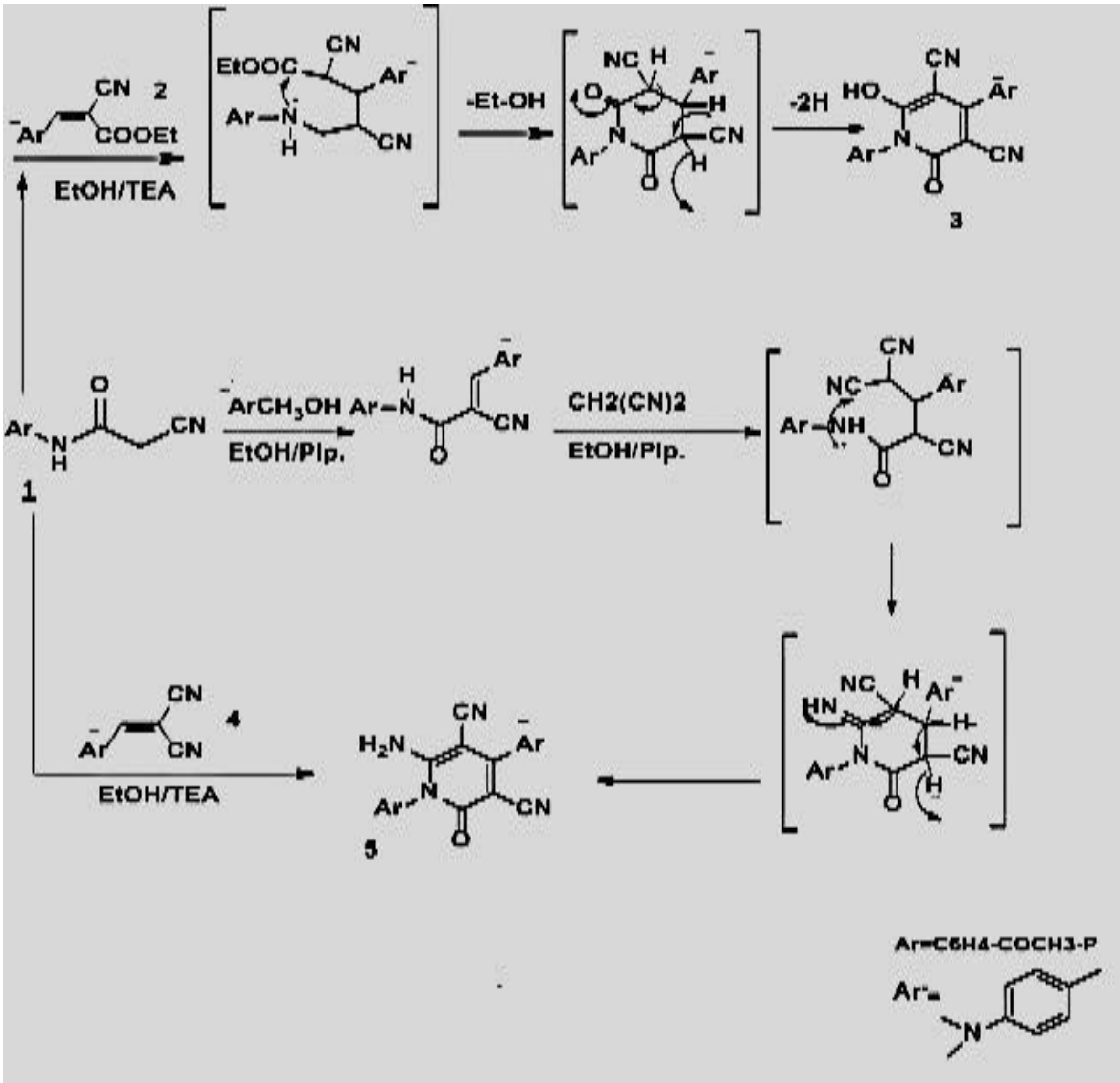

Fig. 1: Steps of synthesis of pyridin-2-one derivatives.

Table 1: characterization of pyridin-2-one derivatives.

Chemical Analysis	1-(4-Acetylphenyl)-4-(4-(dimethylamino)-phenyl)-6-hydroxy-2-oxo-1,2dihydropyridine-3, 5-dicarbonitrile	1-(4-Acetylphenyl)-6-amino-4-(4(dimethylamino)-phenyl)-2-oxo-1,2 dihydropyridine-3, 5-dicarbonitrile
IR (ν_{max}/cm^{-1})	υ/cm^{-1}=3334 (OH), 2219, 2213 (2CN), 1710, 1673 (2CO)	υ/cm^{-1}=3434 (NH_2), 2207, 2204 (2CN), 1700 ($COCH_3$) 1676 (CO)
MS m/z (%)	400 (M^+, 30.56), 333 (38.04), 199 (100.00), 171 (32.81), 117 (22.94), 113 (18.94), 105 (80.44), 87 (15.33), 59 (73.56); Analysis for: $C_{23}H_{18}N_4O_3$ (400.04)	397 (M^+, 3.53), 243 (10.64), 136 (10.05), 97 (55.57), 71 (67.37), 69 (100.00), 67 (36.40), 57 (75.76), 45 (31.20), 42 (17.22); Analysis for: $C_{23}H_{19}N_5O_2$ (397.21)
^{1}H NMR (400MHz, DMSO –d_6)	δ ppm=2.50 (s, 3H, $COCH_3$), 3.33 (s, 6H, $2CH_3$), 6.86-8.11 (m, 8H, Ar-H), 10.36 (s, 1H, OH)	δ ppm=2.50 (s, 3H, $COCH_3$), 3.33 (s, 6H, $2CH_3$), 7.86-8.33 (m, 8H, Ar-H), 10.47 (s, 1H, NH_2).
Melting point	235-237 ^{o}C	260-262 ^{o}C
Elemental Analysis	Calculated: C, 69.34; H, 4.55; N, 14.06%. Found: C, 69.87; H, 4.92; N, 14.90%.	Calculated: C, 69.51; H, 4.82; N, 17.62% Found: C, 69.55; H, 4.42; N, 17.66%.
Colour	Scarlet orange	Dark Yellow powder

3. Synthesis and Characterization of New Nano Additive (cationic Surfactant):

Solid-state reactions of 0.001mole 4-(benzo[d]thiazol-2-yl) aniline (after hydrochloride with concentrated HCL solution) with 0.001mole copper chloride (II) in presence of 0.001mole of CTAB by grinding in the mortar for half an hour until all components mixed well to produce a two-dimensional complex of 5-(benzo[d]thiazol-2-yl)-3-phenyl-2-thioxo-2,3-di hydrothiazol-4-aminium N,N,N trimethyl hexadecan-1-aminium Bromo trichloro cuprate. We investigated the reaction completion by changing the color of a solid mixture from a deep brownish sheet to a deep greenish powder after about a month as shown in Figure (2). The structure of the new additive was proved by Micro elemental analyses (a Vario elementary in a national research center, Cairo, Egypt): C, 50.42; H, 7.06; Br, 10.44; Cl, 13.93; Cu, 8.39; N, 5.50; S, 4.25. We determined that the chemical formula is $C_{32}H_{53}BrCl_3CuN_3S$ and the molecular weight is 761.66. The particle size was measured by transmission electron microscopy (TEM) at a high resolution (200KV), (Fig. 3). The particle size was around 13.4-13.7 nm.

4. Formulation of Pyridin-2-one Derivatives:

A formulation is a manufacturer's process of mixing an active ingredient with adjuvants and dilution solvents. The aim of formulating an active ingredient to ease their application, allows a small amount to be mixed with a larger amount of adjuvants to cover a large area and provides the best stability in the storage. There are two general types of adjuvants pesticides: formulation and spray adjuvants. in the formulation process, we must consider the following: differences in the individual pesticides, differences in the adjuvants (surfactants), differences in solvents (O/W), differences in plant surfaces, and differences in the type of an environment (Foy, 2018). we were mixed 0.1 gm of 5-(benzo[d]thiazol-2-yl)-3-phenyl-2-thioxo-2,3-dihydrothiazol-4-aminiumN, N,N trimethyl hexadecan-1-aminium Bromo trichloro cuprate (additive) to each stander of pyridin-2-one derivatives in ethanol/water solvent. Also, the tested pesticide Congest 15% CS (traditional) was mixed with the same amount in recommended concentration.

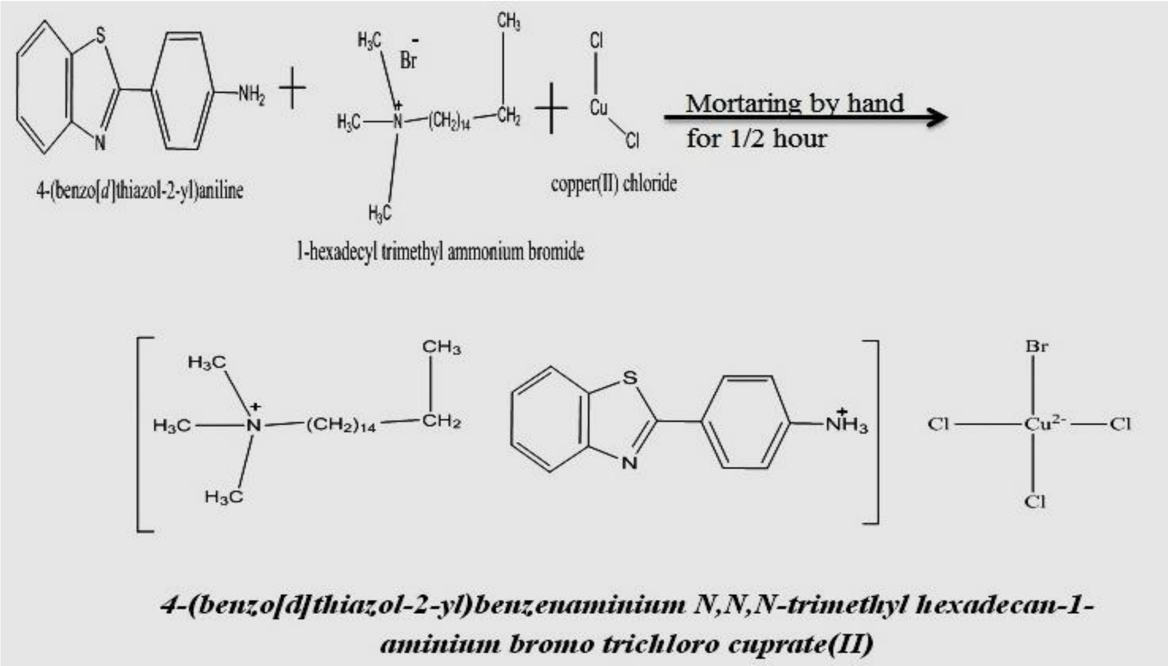

Fig. 2: Steps of synthesis of nano additive (cationic Surfactant).

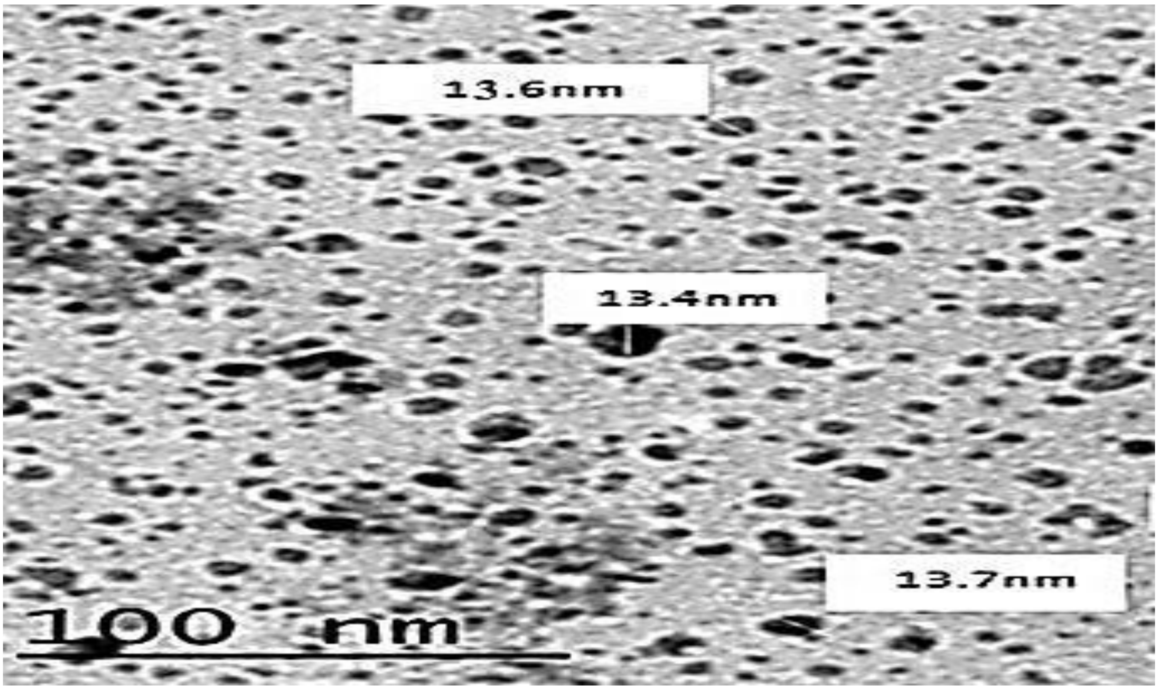

Fig. 3: TEM image of nano additive (cationic Surfactant).

***5.* Measurement of Acidity of Tested Solutions**:

The acidity of formulations is determined by a Jeway 3510 pH Meter with an electrode system. The acidity measurements are shown the effect of adding the cationic nano additive to pyridin-2-one derivatives solutions and to traditional tested pesticide solution (Congest15%CS) on changing pH values, as shown in Table (2).

Table 2: pH values of tested solutions.

Compound Name	*pH*
Congest 15% CS (45ppm)	7.33
Congest 15% CS (45ppm) + Additive	6.22
1-(4-Acetylphenyl)-4-(4-(dimethylamino)-phenyl)-6-hydroxy-2-oxo-1,2dihydropyridine-3, 5-dicarbonitrile (500ppm)	*7.13*
1-(4-Acetylphenyl)-4-(4-(dimethylamino)-phenyl)-6-hydroxy-2-oxo-1,2dihydropyridine-3, 5-dicarbonitrile(500ppm) + Additive	*5.90*
1-(4-Acetylphenyl)-6-amino-4-(4(dimethylamino)-phenyl)-2-oxo-1,2 dihydropyridine-3, 5-dicarbonitrile(500ppm)	*6.98*
1-(4-Acetylphenyl)-6-amino-4-(4(dimethylamino)-phenyl)-2-oxo-1,2 dihydropyridine-3, 5-dicarbonitrile(500ppm) + Additive	*3.26*
Additive: 5-(benzo [d] thiazol-2-yl)-3-phenyl-2-thioxo-2,3- dihydrothiazol aminium N,N,Ntrimethyl hexadecan-1-aminium bromo trichloro cuprate	*5.02*

6. Studding of the Acaricidal Activity:

***6.1.* Growing of Two-Spotted Spider Mite**:

In season 2021/2022, The cotton seeds were planted at 1-2 cm deep in Plastic bags containing soil with peatmus inside PPRI, ARC, Dakahlia, Egypt. Mites and T. urticae were reared and collected from cotton plants. The cotton Mites were transferred with cotton leaves and moistened daily in the lab with wet cotton to avoid disc dryness and were covered to prevent mite escape.

6.2. Evaluation of the Acaricidal Activity of The Applied Insecticide Formulation Prepared Pyridin-2-One Derivatives (A.I) And Their Modified Mixtures with The Applied New Surfactant:

Five concentrations of 1-(4-Acetylphenyl)-4-(4-(dimethylamino)-phenyl)-6-hydroxy-2-oxo-1,2 dihydropyridine-3, 5-dicarbonitrile.(3) (9.25,37.5,125, 250 and 500ppm) , from 1-(4-Acetylphenyl)-6-amino-4-(4-(dimethylamino)-phenyl)-2-oxo-1,2 dihydro-pyridine-3, 5-dicarbonitrile (5) (12.5, 25, 50, 100 and 200 ppm) and from Congest 15% CS (5,15,25,35 and 45ppm) and their modified mixture solutions with 5- (benzo[d]thiazol-2-yl)- 3-phenyl-2-thioxo -2,3-dihydrothiazol- 4-aminium-N,N,N trimethyl hexadecan-1-aminium Bromo trichloro cuprate (new synthetic cationic surfactant additive , 0.1g/100ml water adding to their stock solutions) were applied; leaves of cotton plant were dipped in each concentration for five seconds. Leaves were divided into five replicates. the leaves were dipped in clean water as an untreated check (control). The leaves were transferred to clean wide plastic dishes and 10 two-spotted spider mites, *T. urticae* Koch transferred to the wide plastic dishes, which were then covered. and that replicate four times in each concentration. After 6,24,48 hours the spotted spider mite was counted.

6.3. Statistical analysis:

The mortality percentages, lethal concentration (LC_{50}, LC_{90}), lethal time (LT_{50}), and), X^2 and r were calculated and plotted by LDP line program according to Abbott's formula (Abbott, 1925and Finney, 1971). The toxicity index (Ti) was determined by using Sun,s equation (1950) as follows:(Ti= (LC_{50} of the most effective compound/ LC_{50} of the less effective compound) X100). The data were analyzed by using Anova (one-way) to calculate the significant difference (LSD, P=0.05).

RESULTS AND DISCUSSION

1. The Relative Acaricidal Activity of Congest 15% CS and Their Modified Formulation Against *T. urticae* Koch on Cotton Plants Under Semi-Field Conditions:

The obtained results in Table (3) and Figure (4) against two-spotted spider mite show that Congest 15% CS showed the $LC_{50}$of 19.59ppm. However, LC_{90} reached 63.83 ppm while the results of the acaricidal activity data of Congest 15% CS with cationic surfactant mixture has most acaricidal activity than Congest 15% CS only solution. The LC_{50} and LC_{90} reached 0.43and 4.02 respectively. In Table (4) and Figure (5), The relationship between the mean mortality percentage of two-spotted spider mite and time (hours)showed the effect of adding nano cationic additive on congest 15% CS (LC_{50s}). Adding additive, 5-(benzo[d]thiazol-2-yl) -3-phenyl-2-thioxo -2,3-dihydrothiazol -4-aminiumN, N,N trimethyl hexadecan-1-aminium Bromo trichloro cuprate decreased the lethal time of mortality. The time recorded for 90% mortality percentage for congest 15% CS pesticide was 112 hours (R^2=0.79), while by adding an additive to its modified solution, the time was reduced to only19hour (R^2=0.98).

***2.* The Relative Acaricidal Activity of Pyridin-2-one Derivatives (a.i) and their Modified Formulations:**

The obtained results in Table (3) and Figure (4) against *T. urticae Koch* show that 1-(4-Acetyl phenyl) -4- (4-(dimethyl amino)-phenyl)-6-hydroxy-2-oxo-1,2 dihydropyridine-3, 5-dicarbonitrile. (3) (a.i) with the synthetic adding cationic surfactant has most significant acaricidal activity than its individual solution. LC_{50} value decreases from (28.27 to 5.17ppm) and LC_{90} value decreases from (331.15 to 97.26 ppm). Also, for 1-(4-Acetylphenyl)-6-amino-4-(4-(dimethylamino)-phenyl)-2-oxo-1,2 dihydro- pyridine-3, 5-dicarbonitrile (5). (a.i) with the synthetic adding cationic surfactant has most insecticidal activity than its individual solution. LC_{50} value decreases from (28.27 to 5.17ppm) and LC_{90} value decreases from (331.15 to 97.26 ppm). Also, the acaricidal activity of the two new pyridin-2-one derivatives (a.i) with the new cationic synthetic surfactant is more effective than traditional pesticide; Congest 15% CS. Mites treated with Congest 15% CS had a slower lethal effect, as mortality values were 10, 30, 63.3,70 and 86% after 24 hours reached to 36.7, 46.7, 73.3, 86.7 and 90% after 72 hours for concentrations mentioned before, fig. (1).while pyridin-2-one derivative (1) tested against two-spotted spider mite had a moderate lethal effect, as mortality values were 23.3, 46.7, 73.3, 83.3 and 96.7% after 24 hours reached to 56.7, 70, 89.7 and 98.3 after 36 hours for lower concentrations and 100% after 24 hours for higher applied *concentration*. For tested pyridin-2-one derivative (2) had a highly significant lethal effect, as mortality values were 23.3, 46.7, 73.3, 83.3 and 96.7% after 24 hours reached 56.7, 70, 89.7 and 98.3 after 36 hrs. for lower concentrations and 100% after 24 hours. After adding the new tested synthetic cationic surfactant (5- (benzo [d] thiazol-2-yl) -3-phenyl -2- thioxo -2,3-dihydrothiazol -4-aminium N,N,N trimethyl hexadecan-1-aminium Bromo trichloro cuprate) to the new active ingredient pyridin-2-one derivatives, the mortality values increased to (46.7, 56.7, 86.7 and 96.7% after 12 hours and all tested concentrations reached to 100% mortality percentage after 24 hours) by applied pyridin-2-one derivative (1) with the new additive. The mortality percentage reached the maximum by adding pyridin-2-one derivative (2) with the new additive, it higher increased to (53.3, 66.7, 76.7, 96.7 and100 % after only 6 hours) and all tested concentrations reached 100% mortality percentage after 18hrs. As the calculated LC_{50} of the tested two pyridin-2-one derivatives with the new additive (Table 2) at 24hours against two-spotted spider mite, *Tetranychus urticae Koch* with a toxicity index (Ti= 37.96 and 100%), with LC_{50}values of (5.17 and 1.96ppm). The effectiveness of the two tested pyridin-2-one derivatives with the new additive on *T. urticae* was the most than Congest 15% CS pesticide (Ti= 10.01% with

LC_{50}value of 19.59 ppm) and then their solutions without the additive with a toxicity index (Ti= 6.93 and 8.25%, with LC_{50}values of 28.27and 23.77ppm) respectively. The relationship between the mean mortality percentage of two-spotted spider mites and time (hours: hrs) showed the effect of adding nano cationic additive on pyridin-2-one derivatives. Adding additive, 5-(benzo[d]thiazol-2-yl) -3-phenyl-2-thioxo -2,3-dihydrothiazol -4-aminiumN, N,N trimethyl hexadecan-1-aminium Bromo trichloro cuprate decreased the lethal time of mortality as showed in Table(4) and Figure (6). The lethal time for 90% mortality of pyridin-2-one derivatives (1,2) decreased respectively from (52hrs,45hrs (R^2=0.96)) to (37 hrs (R^2=0.97),15 hrs (R^2=0.897)) after formulated with the tested nano additive.

The addition of new nano cationic surfactant as an additive formulation increases the effectiveness by changing the physicochemical properties of the water and that is observed by changing pH values as shown in Table (2). The increase in the acidity of formulated indicates an increase in the positive charge of spray solution, thus increases of the attraction between spray solution and target plants that have a negative charge on leaves surface and so, increasing the acaricidal efficiency (Rawi, *et al.*,2011). Formulation adjuvants are applied to increase the penetration of active ingredients or pesticides into the target plant, but their penetration varies with different adjuvants, active ingredients and plant species (Wanga, and Liu, 2007).

Table 3: Acaricidal Activity with statistical values and lethal concentrations (L_C;ppm) of pyridin-2-one derivatives, Congest 15% CS and their modified formulation with new cationic additive**.**

Treatment	Conc. (ppm)	Mean Mortality %	LC_{50} (ppm)	LC_{90} (ppm)	Slope	r	X^2	Toxicity index (Ti)	LSD 0.05
Congest 15% CS	*5*	*10^d*	19.59	63.8	2.50±0.4075	0.979	2.189	10.01	*1.73*
	15	*30^c*							
	25	*63.3^b*							
	35	*70^b*							
	45	*86.7^a*							
pyridin-2-one (1)	*9.25*	*23.3^d*	28.27	331.1	1.20±0.1838	*0.974*	*2.257*	6.93	*1.39*
	37.5	*60^c*							
	125	*73.3^b*							
	250	*83.3^b*							
	500	*96.7^a*							
pyridin-2-one (2)	*12.5*	*23.3^c*	23.77	109.8	1.93±0.3214	0.9798	2.474	8.25	*1.25*
	25	*63.3^b*							
	50	*70^b*							
	100	*86.7^a*							
	200	*96.7^a*							
pyridin-2-one (1)+ Additive	*4.5*	*46.7^d*	5.17	97.3	1.01±0.1422	0.9815	0.714	37.96	*0.73*
	18.5	*73.3^c*							
	37.5	*80^c*							
	75	*90^b*							
	125	*97.5^a*							
pyridin-2-one **(2)+ Additive**	*0.82*	*16.7^e*	1.96	6.5	2.45±0.3605	0.9980	0.174	100	*0.94*
	1.65	*43.3^d*							
	3.12	*70^c*							
	6.25	*90^b*							
	12.5	*96.7^a*							
P	0.000 ***								

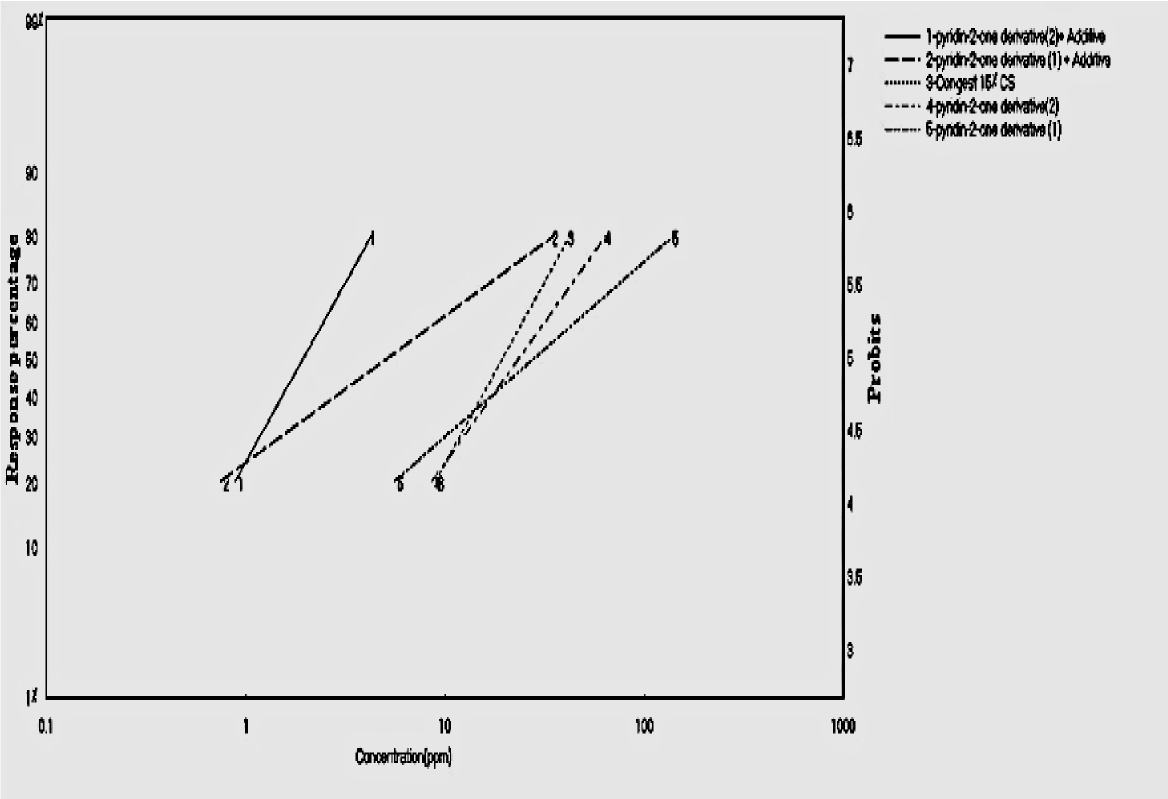

Fig. 4: Acaricidal Activity of Congest 15% CS and pyridin-2-one derivatives (a.i) and their modified formulation.

Table 4: Acaricidal Activity with a lethal time (L_T; hours) of pyridin-2-one derivatives, Congest 15% CS and their modified formulation with a new cationic additive.

Treatment	L_{T50} (hours)	L_{T90} (hours)	Slope	X^2	R	LSD 0.05
Congest 15% CS	30^c	112^e	2.24±0.3250	7.143	0.9505	1.26
pyridin-2-one (1)	17^b	52^d	2.66±0.3663	1.666	0.9881	
pyridin-2-one (2)	14^b	45^c	2.57±0.3172	5.445	0.9686	
pyridin-2-one (1)+ Additive	10^a	37^b	2.24±0.3235	3.297	0.9653	
pyridin-2-one (2)+ Additive	5^a	15^a	2.65±0.4706	1.318	0.9784	

Where, pyridin-2-one (1): **1-(4-Acetylphenyl)-4-(4-(dimethylamino)-phenyl)-6-hydroxy-2-oxo 1,2dihydropyridine-3, 5-dicarbonitrile**.
pyridin-2-one (2): **1-(4-Acetylphenyl)-6-amino-4-(4(dimethylamino)-phenyl)-2-oxo-1,2 dihydropyridine-3, 5-dicarbonitrile**.
Additive cationic surfactant: 5- (benzo [d] thiazol-2-yl) -3-phenyl -2- thioxo -2,3-dihydrothiazol -4-aminium N,N,N trimethyl hexadecan-1-aminium bromo trichloro cuprate.

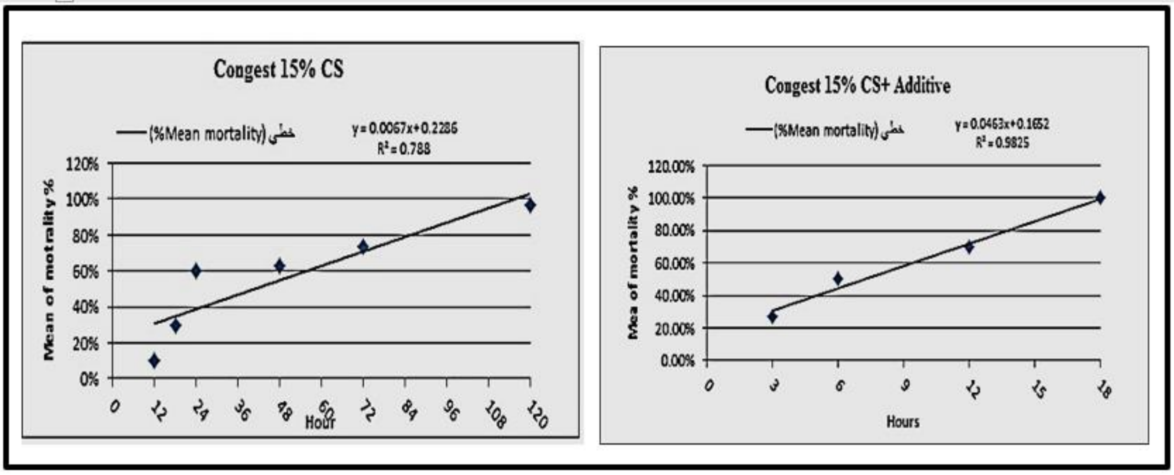

Fig. 5. The relationship between the mean mortality percentage of two-spotted spider mites treated with Congest 15% CS and their modified formulation with new cationic additive (LC_{50s}) and time (hours).

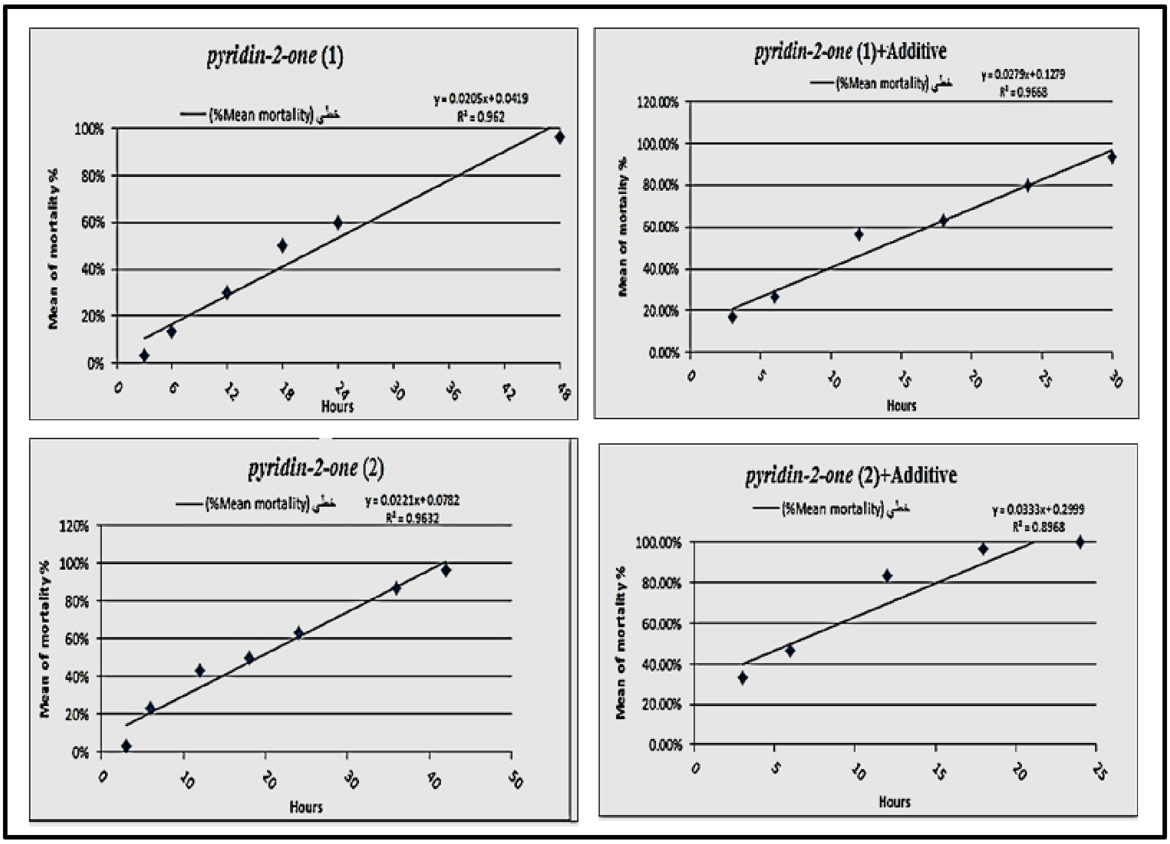

Fig. 6. The relationship between the mean mortality percentage of two-spotted spider mites treated with pyridin-2-one derivatives and their modified formulation with new cationic additive (LC_{50s}) and time (hours).

Conclusion

The acaricidal activity of two pyridin-2-one derivatives and their modified formulations were affected by their chemical structure and their formulated additive. The presence of the carbonitrile group and thioxo group in their structures increased the electron withdrawing process; hence increasing the acaricidal activity. The synthetic nano additive-enhanced the toxicity of derivatives against two-spotted spider mites; *T.urticae*. Applied new additive increases the adsorption of a target plant foliage, to active ingredients. The penetration of two pyridin-2-one derivatives is regarded as the change in physicochemical properties of the active ingredients. This chemical additive decreases the number of active compounds needed, so decreasing pollution and cost.

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ARABIC SUMMARY

تعزيز نشاط مستحضرات مشتقات بريدين-2-اون باستخدام مادة نانو خافضة للتوتر السطحي على العنكبوت الأحمرذو البقعتين الذي يغزو القطن في مصر.

نيرة سمير المصري، *، هبة محمد نصر، شرين عبد الرحمن شومان
معهد وقاية النباتات- مركز البحوث الزراعية- الدقي- مصر.

خلال عام 2022/2021، تمت دراسة تأثير اثنين من مشتقات بريدين-2-اون اللذين ينتميان إلى مركبات السيانو أسيتاميد وتركيباتهما المعدلة للسيطرة على العنكبوت الأحمرذو البقعتين (Tetranychus urticae Koch). قمنا بتحضير وتوصيف مشتقات بريدين-2-اون (كمكونات فعاله نشطة). تم دراسة التركيب الكيميائي للمشتقات بواسطة طيف الأشعة تحت الحمراء، أطياف الكتلة، طيف الرنين المغناطيسي النووي ونقطة الانصهار. تم تحضير خمسة تركيزات من كل من (1- (4-أسيتيل فينيل) -4- (4- (ديميثيلامينو) -فينيل) -6-هيدروكسي -2-أوكسو-2،1 ثنائي هيدرو بيريدين-3،5 ديكاربونيتريل) و من (1- (4-أسيتيل فينيل) -6-أمينو-4- (4- (ديميثيلامينو) -فينيل) -2-أوكسو-2،1 ديهيدرو بيريدين -3، 5- ديكاربونيتريل). و خمسة تركيزات من محلول مبيد الكونجيست (15%) ومحاليلهم المخلوطة المعدلة مع المادة المنشطة السطحية المحضرة في حجم النانو (5- (بنزو [د] ثيازول-2-يل- 3-فينيل-2-ثيوكسو -3،2-ثنائي هيدروثيازول -4-أمينوم N، N، N ثلاثي ميثيل هيكساديكان-1-أمينوم برومو ثلاثي كلورو كبريتات (0.1 جم)) تحت ظروف شبه الحقلية ضد العنكبوت الأحمرذو البقعتين. تم تعديل المشتقين باستخدام المادة النانو المنشطة للسطح لزيادة تأثير السمية على العنكبوت الأحمر (T.urticae Koch). أيضًا، تم إجراء تأثير السمية لمحلول مبيد الكونجيست (كمبيد آفات تقليدي) ومحلولها المعدل بواسطة المادة الخافضة للتوتر السطحي الجديدة المختبرة في ظل ظروف شبه حقليه. أظهرت النتيجة أن مستخلصي بريدين-2-اون مع اضافه ماده النانو السطحي كانت أكثر فاعلية من محلول مبيد الكونجيست (15%). تم حساب قيم التركيز النصف المميت (LC_{50}) لمحلول مبيد الكونجيست (15%) ومشتقى بريدين-2-اون وكذلك الوقت النصف المميت (LT_{50} ؛ ساعات) حيث كان هناك انخفاض معنوي بعد إضافة ماده النانو السطحية إلى المبيد الذي تم اختباره والمواد الكيميائية (مشتقي بريدين-2-اون) على التوالي.